Novel Electron Donors for Organic Conductors. Benzo[c]thiophene-Extended Analogues of Methylene-, Ethylene-, and Propylenedithiotetrathiafulvalene

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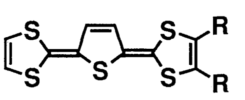
(Received September 8, 1994)

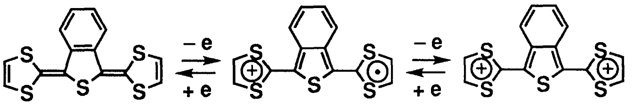
Three alkylenedithio derivatives of 1,3-bis(1,3-dithiol-2-ylidene)-1,3-dihydrobenzo[c]thiophene (BDTBT) have been synthesized. These donors exhibited an electron-donating ability near to that of tetrathiafulvalene and afforded a very stable radical cation. The powdered tetracyanoquinodimethane complex of the methylenedithio derivative exhibited a fairly high room temperature conductivity of σ=15 Scm^{-1} and a semiconducting behavior with a very low activation energy of Ea=0.050 eV.

One particular aspect in the synthesis of promising donors for organic metals and organic superconductors is to extend the π-system of donors by replacing the intercyclic C=C bond of tetrathiafulvalene (TTF) with an appropriate π-linking group,[1] since such an extension is very important for attaining high conductivity by reducing the on-site Coulomb repulsion in the dicationic state.[2] More recently, such conjugation-elongated donors have been realized to be quite adequate to the conducting components for high-T_C organic superconductors due to an increase in the thickness of the effective conducting layer.[3] However, those donors extended with an open-chain polyene, phenylene, or naphthalene bridge are generally unstable in the neutral state[1c,4] and tend to give unstable radical cations.[1b,5] It was clarified for the first time by our group that incorporation of a sulfur atom into the linking π-bridge stabilizes significantly the radical cation state,[6] and we have recently synthesized 2,5-bis(1,3-dithiol-2-ylidene)-2,5-dihydrothiophene (BDTT) 1 and its dichalcogeno derivatives 2 and 3,[7] in which the latter two have outer chalcogen atoms to increase the dimensionality of the Fermi surface.

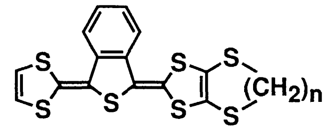


1 : BDTT : R = H
2 : EDT-BDTT : R-R = SCH_2CH_2S
3 : BMT-BDTT : R = SMe

Although **1**, **2**, and **3** are stable in the solid state and gave a stable radical cation, they are powerful donors and in consequence a little air-sensitive in solution. Therefore new BDTT type of extended donors having a somewhat weaker electron donating ability are more favorable for the component of organic conductors. The electron donating abilities of BDTTs might be weakened by condensation of a benzene ring on the 2,5-thienoquinonoid ring, because the linking group takes an unstable benzo[c]thiophene structure, namely *ortho*-quinodimethane structure at the radical cationic stage, as well as the dicationic stage (Scheme 1). From this point of view, we herein report the successful synthesis and electrochemical properties of dichalcogeno derivatives **4**, **5**, and **6** of 1,3-bis(1,3-dithiol-2-ylidene)-1,3-dihydrobenzo[c]thiophene (BDTBT), new entries of the BDTT-type of conjugation-extended donors, and electrical properties of their charge transfer (CT) complexes. The donors **4** and **5** are of especially current interest, because their mother compounds, methylene- and ethylenedithiotetrathiafulvalenes (MDT-TTF and EDT-TTF)[8,9] have produced organic superconductors.



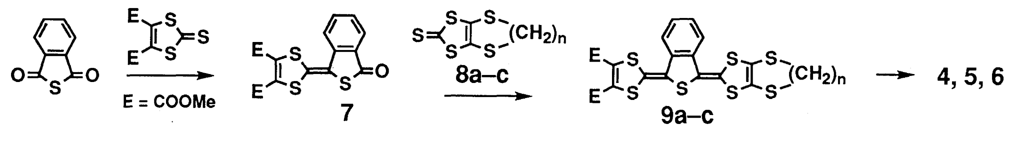
Scheme 1.



4 : MDT-BDTBT : n = 1
5 : EDT-BDTBT : n = 2
6 : PDT-BDTBT : n = 3

The synthetic routes to MDT-BDTBT **4**, EDT-BDTBT **5**, and PDT-BDTBT **6** are outlined in Scheme 2. The cross-coupling reaction of thiophthalic anhydride with an equimolecular amount of 4,5-bis(methoxycarbonyl)-1,3-dithiol-2-thione in the presence of excess of trimethyl phosphite in refluxing benzene gave mono-capped intermediate **7** in 75% yield. Treatment of **7** with 4,5-alkylenedithio-1,3-dithiol-2-thiones **8a**, **8b**, and **8c** in refluxing toluene containing excess trimethyl phosphite afforded bis-capped products **9a** (10%), **9b** (29%), and **9c** (15%), respectively, which were demethoxycarbonylated by heating with lithium bromide monohydrate in hexamethylphosphoric triamide (HMPA) to give **4**, **5**, and **6**, respectively in nearly quantitative yields.[10] The synthetic method reported here provides a mild and short step procedure, that can complement the previous method[7] involving the dehydrogenation of the intermediate with DDQ.

BDTBTs **4**, **5**, and **6** are stable not only in the solid state but also in solution in common organic solvents and showed two well-defined reversible one-electron oxidation waves in the cyclic voltammograms. The electrochemical parameters obtained by the cyclic voltammetry are summarized in Table 1 along with those of TTF and **2** measured under the same conditions. The first oxidation potentials (E_1^{ox}) of **4**, **5**, and **6** are much the same as that of TTF and higher by 0.18—0.19 V than that of **2**, demonstrating that the electron donating ability is weakened as we expected by condensation of a benzene ring on the central thienoquinonoid ring. The second oxidation potentials (E_2^{ox}) of **4**, **5**, and **6** are also higher by 0.17—0.20 V than that of **2**. This is



Scheme 2. a: n=1, b: n=2, c: n=3

Table 1. Electrochemical data of **4**, **5**, **6**, **2**, and TTF, and electrical conductivities of their TCNQ complexes

Donor	Electrochemical property[a]				Conductivity[b] and IR band[c] of the TCNQ complex			
	E_1^{ox}	E_2^{ox}	ΔE^{ox}	log K_{sem}	D : A	σ_{RT} /Scm^{-1}	ν_{CN} /cm^{-1}	ν_{CT} /cm^{-1}
4	+0.36	+0.55	0.19	3.22	1 : 1	15	2177	3000 (br)
5	+0.37	+0.58	0.21	3.56	1 : 1	4.8	2177	3100 (br)
6	+0.37	+0.58	0.21	3.56	2 : 1	4.2×10^{-2}	2177, 2148	3000 (br)
2	+0.18	+0.38	0.20	3.39	3 : 2	3.3	2177	3000 (br)
TTF	+0.37	+0.75	0.38	6.44	—	—	—	—

[a] Potentials are given in V *vs.* SCE and were determined by cyclic voltammetry / 1.0 mM solutions in PhCN with 0.1 M TBAP : 50 mV / sec.
[b] Four-probe method on a compaction pellet. [c] ν_{CN} of TCNQ: 2220 cm^{-1}.

reasonable by considering that the central π-linking group of BDTBTs can acquire an extra destabilization energy by taking an unstable benzo[c]thiophene structure both in the radical cation state and in the dication state as shown in Scheme 1. In consequence, the ΔE^{ox} ($=E_2^{ox} - E_1^{ox}$) values and the semiquinone formation constants (log K_{sem} values) of **4**, **5**, and **6** do not significantly change from the corresponding values of **2**.

MDT-BDTBT **4** and EDT-BDTBT **5** formed 1:1 CT complexes with tetracyanoquinodimethane (TCNQ), whereas PDT-BDTBT **6** formed a 2:1 TCNQ complex, rich in donor component. The oxidation potentials of these three donors are nevertheless almost identical with each other. As shown in Table 1, the room temperature conductivities of the TCNQ complexes of **4** (15 Scm^{-1}) and **5** (4.8 Scm^{-1}) measured on a compressed pellet are 10^3 and 10^2 times higher, respectively, than that of **6**. Probably, a uniform intermolecular face-to-face arrangement of the donor molecules in the stacks would be difficult to attain in the TCNQ salt of **6** since the propylene moiety may take a nonplanar chair-like conformation.[11] As far as we know, the conductivity of the TCNQ complex of **4** is highest among the conductivities reported so far for the powdered CT complexes of conjugation-extended TTF type donors, although similar high conductivities have been reported for the single crystalline TCNQ complexes of ethanediylidene-extended TTF[12] and anthraquinonoid-extended tetramethyl-TTF.[13] The temperature dependence of the conductivity for the powdered TCNQ complex of **4** shows a semiconducting behavior with a very low activation energy of 0.050 eV, suggesting that it might exhibit a metallic conducting behavior in a single crystalline state.

All the complexes of **4**, **5**, and **6** showed a broad absorption band in the IR region at around 3000 cm^{-1} characteristic of an intrastack CT transition[14] in a segregated stack with a mixed valence state. The degree of CT estimated primarily from ν_{CN} values (Table 1) using Chappell's equation is fully ionic with Z=0.97. However, we can believe that the present TCNQ complexes of **4**, **5**, and **6** exist in a partial CT condition on taking account of their high conductivities. Preparations of single crystals of the CT complexes and radical salts with inorganic anions are in progress.

The present work was supported by the grant from the Shorai Foundation for Science and Technology and by the Grant-in Aid for Scientific Research on Priority Area of Molecular Conductors (No. 06243203) and No. 06640674 from the Ministry of Education, Science and Culture.

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10 Selected physical data for **4**: brown microcrystals, mp 162—164 °C; DEI-MS m/z 412 (M^+, 100%); ^{1}H NMR (200 MHz, C_6D_6) δ 3.87 (4H, s, $-SCH_2S-$), 5.51 (1H, d, *J*=6.7 Hz, dithiH-4 or 5), 5.59 (1H, d, *J*=6.7 Hz, dithiH-5 or 4), 7.00 and 7.53 (each 2H, first order AA'XX'). **5**: brown microcrystals, mp 71—72 °C; DEI-MS m/z 426 (M^+, 100%); ^{1}H NMR (400 MHz, C_6D_6) δ 2.21 (4H, s, SCH_2CH_2S), 5.47 (1H, d, *J*=6.4 Hz, dithiH-4 or 5), 5.54 (1H, d, *J*=6.4 Hz, dithiH-5 or 4), 7.03 and 7.55 (each 2H, first order AA'XX'). **6**: brown microcryst, mp 112—114 °C; EI-MS m/z 440 (M^+, 100%); ^{1}H NMR (200 MHz, C_6D_6) δ 1.47 (2H, mc, $-CH_2CH_2CH_2-$), 1.77 (4H, mc, $-SCH_2-$), 5.42 (1H, d, *J*=6.5 Hz, dithiH-4 or 5), 5.49 (1H, d, *J*=6.5 Hz, dithiH-5 or 4), 6.98 and 7.53 (each 2H, first order AA'XX').
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